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(54) Phosphate Compositions for Coating Metal Surfaces

(57) Coatings are formed on iron or steel surfaces by immersing them in a hot acidic solution comprising zinc, phosphate and nitrate and a relatively high content of manganese of at least 0.6 g/l.

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SPECIFICATION Processes and Compositions for Coating Metal Surfaces

Phosphate coatings may be formed on iron and steel surfaces by immersion in acidic phosphating solutions containing zinc, nitrate and phosphate. It is possible to obtain phosphate coatings that are very suitable as a base for lubricants used in cold forming operations. Thus when subsequently treated with a rust preventing oil they give corrosion resistance values similar to those obtainable with electro-deposited metal coatings of, for instance, zinc or cadmium.

When the phosphate coating is to be used in combination with oils and for facilitating cold forming such as, for instance, cold impact forming, it is desirable for the coating to be of fairly high weight, for example 8 to 30 g/m². It is sometimes particularly desirable to have high corrosion resistance. In theory this may be achievable by increasing the weight of the coating and this in theory would also permit higher degrees of shaping or deformation during cold forming operations.

In US Patent Specification 3,268,367 and German Auslegeschrift 12 87 412 processes of forming thick zinc phosphate coatings on iron and steel surfaces are described. In these processes the surfaces are contacted with a nitrate accelerated acidic zinc phosphating solution that includes polycarboxylic acid in which the carbon atom adjacent at least one of the carboxyl groups bears a hydroxyl, amino or carboxylic group. The solution may also contain additives such as nickel, cobalt, lithium, bismuth and manganese in small concentrations of less than 0.5 g/l so as to activate the metal surface that is to be phosphated and promote the deposition of the desired zinc phosphate coatings.

A disadvantage of such processes is that the deposition of thick coatings results in comparatively high consumption of chemicals. Also in some cases, for example with some alloys, there may be problems in trying to deposit coatings of adequate thickness.

It would be desirable to be able to achieve coatings having the desired properties by hot immersion while avoiding or minimising these difficulties.

It is already known to incorporate larger amounts of manganese in acidic phosphating solutions containing zinc and manganese. This is described in British Patent Specification No. 983,924. The compositions described therein are used for cold application, generally cold spraying, and have a ratio of total acidity to free acidity which is preferably from 50:1 to 100:1. The methods described in that specification in general do not give the results desired in some instances, especially when the iron or zinc is to be cold formed, often in combination with a rust preventing oil.

An acidic solution according to the invention suitable for forming phosphate coatings on iron or steel surfaces by hot immersion comprises phosphate, nitrate, zinc and manganese ions and in this solution the amount of manganese is at least 0.6 g/l, the weight ratio Mn:Zn is 1:22 to 0.2, the weight ratio P₂O₅:NO₃ is 1:0.2 to 4.0 and the ratio total P₂O₅:free P₂O₅ is 1:0.2 to 0.8.

A phosphate coating may be formed on an iron or steel surface by immersing the surface in such a solution at a treatment temperature of 50 to 98°C. Preferably the solution has a total acid point number during use of at least 20 points.

The invention can result in the production of zinc-manganese phosphate coatings having, for a given coating thickness, corrosion resistance and cold forming properties superior to those of zinc phosphate coatings made by known methods.

The solution preferably contains at least 1 g/l manganese ions since in general increasing the amount of manganese phosphate improves the properties. In particular its suitability as a base for cold forming operations is improved. If the ratio Mn:Zn is below 1:0.2 then the process is liable to result in incomplete, pitted coatings.

The ratio Mn:Zn is preferably 1:0.8 to 12. It is generally unnecessary to have large amounts of manganese in the composition and so the amount is normally below 25 g/l, preferably below 12 g/l. Particularly suitable amounts are from 2 to 5 g/l.

The solution may contain phosphate in an amount of preferably 15 to 40 g/l P₂O₅ and nitrate in an amount of 5 to 60 g/l NO₃. The ratio P₂O₅:NO₃ is preferably 1:0.3 to 3.

The ratio total P₂O₅:free P₂O₅ is preferably 1:0.25 to 0.7.

The total acid point number is preferably 30 to 90, typically 70 to 80. The total acid point number can be determined by titration of a 10 ml bath sample with 0.1 N NaOH against phenolphthalein as indicator until there is a change from colourless to pink.

The following are examples of suitable solutions.

Examples					
	1	2	3	4	
Zn g/l	11.7	6.08	33.3	10.3	55
Mn g/l	4.28	2.18	3.11	20.2	
P ₂ O ₅ g/l	33.6	28.9	19.3	20.0	
NO ₃ g/l	10.1	8.68	57.7	55.0	
P ₂ O ₅ :NO ₃	1:0.3	1:0.3	1:2.99	1:2.74	
Total P ₂ O ₅ : free P ₂ O ₅	1:0.26	1:0.69	1:0.26	1:0.42	60
Mn:Zn	1:2.7	1:2.8	1:10.7	1:0.5	

In order to activate the iron or steel surface it may be desirable to include one or more types of metal ions, generally selected from nickel, cobalt and copper. Such metal ions may be added in an amount of 0.02 to 0.1 g/l. These metal activators may be introduced as, for instance nitrates or sulphates.

- 5 When it is desired to increase further the weight of the coating it is preferred to include simple and/or complex fluoride in the solution. Suitable fluorides are NaF, NaHF₂ and/or Na₂SiF₆. 5

The inclusion of condensed phosphates is preferred when it is desired to reduce the weight of the coating.

- 10 It is in the nature of nitrate accelerated phosphating solutions that iron (II) ions accumulate in the bath during use so that the total acid point number decreases and it is preferable to ensure that it does not decrease to such an extent that the bath acquires a value below the preferred limits quoted above. In order to prevent deterioration in results replenishment of the bath during use is necessary. In the invention the replenishment preferably provides zinc, manganese, phosphate and nitrate ion in the following ratios. 10

- 15 $P_2O_5:NO_3=1:0.3$ to 2.0
Total P_2O_5 -free $P_2O_5=1:0.3$ to 0.8
Mn:Zn=1:2 to 80. 15

The solution may be made in conventional manner from the individual ingredients or by appropriate dilution of a concentrate.

- 20 The surfaces to be treated should be free from grease and scale and/or rust. Degreasing may be effected by, for example, aqueous alkaline cleaners containing surface active substances. Descaling is preferably effected using sulphuric or hydrochloric acid. After cleaning and/or pickling the surfaces should be rinsed well with water. 20

- 25 Before phosphating the surfaces may be pre-rinsed in known manner, for example with titanium orthophosphate or manganese orthophosphate suspensions in water in order to form finely crystalline coatings. However it has been found in practice that such prerinses may not be required and that instead merely prerinsing with water at a temperature of 50 to 98°C often activates the surface sufficiently. 25

- 30 Contact between the surface and the acidic phosphating solution of the invention is effected by immersion, with the solution being at a temperature of 50 to 98°C. Immersion times of 5 to 15 minutes are generally suitable. 30

- 35 The accumulation of iron (II) during use is not, in itself, detrimental to the process. However in some instances, for instance with high nitrate concentrations or high bath temperatures, it will be found that iron (II) does not accumulate as a result of its oxidation during iron (III) and this also is satisfactory. Naturally replenishment is necessary in the manner described above. 35

Depending on the solution used, the conditions of application and the particular iron alloy surface being treated the weight of the zinc-manganese phosphate coatings obtained is generally from 5 to 30 g/m².

- 40 After phosphating the surface may be rinsed with water, after treated if necessary, and optionally dried. When corrosion protection is particularly required the after treatment may involve, for example, treatment with chromic acid solution followed by treatment with an emulsion of a corrosion preventing oil. When cold forming properties are particularly required the after treatment may include application of soap solution. 40

- 45 The following are some examples of processes in accordance with the invention and in these baths C, E, F and G are further examples of compositions according to the invention. 45

Example 5

Steel screws were treated as follows:

- a) Pickling in 15% sulphuric acid with an addition of a pickling inhibitor at 60°C and for an immersion time of 10 minutes.
b) Rinsing with cold water.
c) Rinsing with water at a temperature of 60°C.
d) 10 screws were phosphated in each case by immersion for 10 minutes in phosphating baths A, B and C. 50

		Bath A Zn phosphate	Bath B Zn phosphate	Bath C Zn-Mn phosphate	
55	Zn g/l	20.7	26.8	12.7	55
	Mn g/l	—	—	10.8	
	Ni g/l	0.03	0.03	0.03	
	P_2O_5 g/l	24.8	20.3	19.4	
60	NO_3	26.3	39.6	37.9	60
	Total acid points	75	75	70	
	$P_2O_5:NO_3$	1:1.06	1:1.95	1:1.95	

	Total P ₂ O ₅ :free P ₂ O ₅	1:0.40	1:0.36	1:0.36	
	Mn:Zn	—	—	1:1.2	
5	Bath temperature °C	98	75	75	5
	Coating weight g/m ²	24.9	18.6	15.1	

e) Rinsing with cold water.

f) After-rinsing in fully desalted water with the addition of 0.5 g/l of sodium bichromate at 80°C.

g) Treatment with a 13% emulsion of a corrosion preventing oil at 60°C.

10 h) Oven drying at 70°C. 10

The screws were then tested by the salt spray test according to DIN 50021 SS. 10 screws were tested using each of the three baths A, B and C. After a test period of 72 hours, 50% of the screws treated with baths A and B were rusty but all 10 screws treated with bath C had not been attacked, although the weight of the coating was less than in the case of baths A and B.

15 **Example 6** 15

Cold impact formed parts were treated as follows:

a) Pickling in 15% hydrochloric acid with the addition of a pickling inhibitor at room temperature and with a treatment time of 10 minutes.

b) Rinsing with cold water.

20 c) Rinsing with water at a temperature of 75°C. 20

d) 100 cold impact formed parts were treated in each case for 10 minutes by immersion in phosphating baths D and E.

		<i>Bath D Zn phosphate</i>	<i>Bath E Zn-Mn phosphate</i>	
25	Zn g/l	20.5	18.7	25
	Mn g/l	—	5.8	
	Ni g/l	0.2	0.03	
	P ₂ O ₅ g/l	24.9	19.4	
	NO ₃ g/l	29.3	37.9	
30	Total acid points	80	70	30
	P ₂ O ₅ :NO ₃	1:1.2	1:1.95	
	Total P ₂ O ₅ :free P ₂ O ₅	1:0.53	1:0.36	
	Mn:Zn	—	1:3.2	
	Bath temperature °C	98	75	
35	Coating weight g/m ²	18.3	17.5	35

e) Rinsing with cold water.

f) Treatment in a 5% soda soap at 73°C and for an immersion time of 5 minutes.

g) Drying in air through the own heat of the parts.

40 The parts were extruded back to form tubes. In the case of those parts which had been treated in bath D, the tubes had about 80% scoring and the surface had a metallicly bright appearance. In the case of those parts which had been treated in bath E, no scoring could be detected and the surface was grey, which points to a considerable residual phosphate coating. 40

Example 7

Steel sheets of quality USt 1405 m were treated as follows:

45 a) Cleansing in a strongly alkaline aqueous cleansing agent at 95°C and for an immersion time of 15 minutes. 45

b) Rinsing with cold water.

c) Pickling in H₂SO₄, 20% with the addition of a pickling inhibitor, at 65°C and for an immersion time of 10 minutes.

50 d) Rinsing with cold water. 50

e) Phosphating at 75°C and for an immersion time of 10 minutes in baths F and G.

f) Rinsing with cold water.

The composition of baths F and G is given in the following Table below. The total acid point number of the baths was 90 points in each case.

55 After a throughput of 0.2 m² of sheet surface per litre of bath solution in each case, the baths were replenished to point constancy with the replenishing concentrates given in the Table. 55

On commencement of throughput and after the throughput of 4 m² of steel surface per litre of bath solution, sample sheets were set aside for determining the coating weight and for testing corrosion by the salt spray test according to DIN 50021 SS.

60 The sheets for corrosion testing were treated beforehand with a 15% emulsion of a corrosion preventing oil and then dried in an oven at 70°C. 60

Table				
		Bath F	Bath G	
5	Zn g/l	22.3	22.6	5
	Mn g/l	2.1	8.11	
	Ni g/l	0.04	0.03	
	P ₂ O ₅ g/l	29.8	24.3	
	NO ₃ g/l	31.6	50.4	
10	Total acid point number	90	90	10
	Total P ₂ O ₅ :free P ₂ O ₅	1:0.40	1:0.50	
	P ₂ O ₅ :NO ₃	1:1.06	1:2.07	
	Mn:Zn	1:10.6	1:2.79	
		Replenishing concentrate for Bath F	Replenishing concentrate for Bath G	
15	Zn %	12.6	11.8	15
	Mn %	0.31	1.88	
	Ni %	0.03	0.03	
	P ₂ O ₅ %	25.8	22.9	
	NO ₃ %	11.4	17.7	
20	Total P ₂ O ₅ :free P ₂ O ₅	1:0.41	1:0.55	20
	P ₂ O ₅ :NO ₃	1:0.44	1:0.77	
	Mn:Zn	1:40.6	1:6.3	
	Coating weight at beginning	15.6 g/m ²	18.2 g/m ²	
25	Coating weight after 4 m ² /l	16.2 g/m ²	19.0 g/m ²	25
	Rust after 72 hour salt spray test according to DIN 50021 SS			
30	at the beginning	0%	0%	30
	after 4 m ² /l	0%	0%	

It can be perceived clearly that, as a result of the preferred form of the replenishment, even after the throughput of 4 m²/l the phosphating baths lead to coatings which have retained their good properties.

- 35 **Claims** 35
1. An acidic solution suitable for forming phosphate coatings on iron or steel surfaces by hot immersion and comprising phosphate, nitrate, Zn and Mn ions and in which the amount of Mn is at least 0.6 g/l, the weight ratio Mn:Zn is 1:22 to 0.2, the weight ratio P₂O₅:NO₃ is 1:0.2 to 4 and the ratio total P₂O₅:free P₂O₅ is 1:0.2 to 0.8.
 - 40 2. A solution according to claim 1 containing at least 1 g/l Mn. 40
 3. A solution according to claim 1 or claim 2 in which the weight ratio Mn:Zn is 1:0.8 to 12.
 4. A solution according to any preceding claim containing simple or complex fluoride.
 5. A solution according to any preceding claim having a total acid point number of at least 20 points and in which the weight ratio P₂O₅:NO₃ is 1:0.3 to 3 and the ratio total P₂O₅:free P₂O₅ is 1:0.25 to 0.7.
 - 45 6. A method of producing a phosphate coating on an iron or steel surface comprising immersing the surface in a solution according to any preceding claim at a treatment temperature of 50 to 98°C.
 7. A method of producing a phosphate coating on an iron or steel surface comprising immersing the surface in a solution according to claim 5 at a treatment temperature of 50 to 98°C.
 - 50 8. A method according to claim 6 or claim 7 in which the solution is replenished during use by replenishment containing zinc, manganese, phosphate and nitrate ions in the ratios by weight 50
- P₂O₅:NO₃=1:0.3 to 2.0
 Total P₂O₅:free P₂O₅=1:0.3 to 0.8
 Mn:Zn=1:2 to 80.
- 55 9. A solution according to claim 1 substantially as herein described. 55
 10. A method according to claim 6 substantially as herein described.